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THE ACTION OF MANGANESE UNDER ACID AND NEUTRAL SOIL CONDITIONS.

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INTRODUCTION.

Investigations of the action of manganese on plants and soils have been conducted by the Office of Soil-Fertility Investigations both in the laboratory and in the field for several years.

Manganese is universally found in soils and plants. Robinson,[1] who examined 26 American soils, found the content of manganese (MnO) to be from 0.01 to 0.51 per cent, the average being 0.071 per cent, and Kelley [2] found in Hawaiian soils amounts varying from less than 0.1 to 9.74 per cent Mn_3O_4.

A number of investigators have studied the effect of manganese on plants in both water and soil cultures, and from the evidence at hand it seems that in most cases manganese in small amounts exercises a stimulating action on growth. A general review of the literature on the subject has been given in former papers of members of

[1] Sullivan, M. X., and Robinson, W. O. Manganese as a fertilizer. U. S. Dept. Agr., Bur. Soils Circ. 75, 3 p. 1913.

[2] Kelley, W. P. The influence of manganese on the growth of pineapples. Hawaii Agr. Exp. Sta. Press Bul. 23, 14 p., n. d.

——— Manganese in some of its relations to the growth of pineapples. *In* Jour. Indus. and Engin Chem., v. 1, no. 8, p. 533-538. 1909.

Note.—The results given in this bulletin throw further light on the effect of this catalytic fertilizer under various soil conditions. That its effect is dependent on the reaction of the soil is demonstrated. The bulletin is of interest to scientific investigators, to manufacturers of catalytic fertilizers, and to those growers whose technical training induces them to experiment with new substances to increase or control crop production.

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the staff of the Office of Soil-Fertility Investigations and others,[1] so its repetition here is not deemed necessary.

Working with soil extracts [2] from poor, unproductive soils, manganese salts were found to increase the oxidizing power of the plant roots grown therein and increased the growth of the plants. With extracts from good, fertile soils the oxidative power of the plants was increased, but it was not attended by an increase in growth. This was attributed to excessive oxidation in the soil solution. The plant tips and leaves themselves showed indications of this excessive oxidation. Similar results were obtained with soil in pots. The poor, unproductive soils were improved by manganese, while good soils were not further benefited. The best results were secured with small amounts varying from 5 to 50 parts per million of the element manganese.

Schreiner and Sullivan [1] have further pointed out that the oxidative power of the soil is dependent in part on the nature of the organic matter. Thus, when salts of manganese, iron, calcium, etc., were added to soil of slight oxidative power, oxidation was but slightly increased until certain kinds of organic matter, such as citric, malic, tartaric, and glycolic acids or their salts, were added, when marked improvement in oxidation took place.

EFFECT OF MANGANESE ON ARLINGTON SOIL UNDER ACID CONDITIONS.

Field tests with manganese sulphate were inaugurated on the experiment farm of the Department of Agriculture at Arlington, Va., in 1907. The results secured from 1907 to 1912 have already been published.[2] The experiment has been continued with some modification, and the additional data throw considerable light on the action of manganese in soils of this character. The soil in which these experiments were made is a silty clay loam, low in organic matter. The physical condition of the soil is rather poor, and great care had to be practiced in cultivation to keep it in a good physical condition. The ground is level and has surface drainage, and the soil throughout these manganese plats and their controls is uniform, so the results obtained should not be considered as unduly influenced by irregularities due to nonuniformity of the soil in different plats. The soil is of an acid nature.

The ground on which these experiments were made consists of two parallel strips of land, each 1 rod wide and separated by a 3-foot path. Each strip is divided into seven plats of 1 square rod, with

[1] Schreiner, Oswald, and Sullivan, M. X. Studies in soil oxidation. U. S. Dept. Agr., Bur. Soils Bul. 73, 57 p. 1910.

Kelley, W. P. The function and distribution of manganese in plants and soils. Hawaii Agr. Exp. Sta. Bul. 26, 56 p. 1912.

[2] Skinner, J. J., Sullivan, M. X., et al. The action of manganese in soils. U. S. Dept. Agr. Bul. 42, 32 p. 1914.

paths 2½ feet wide separating the plats. One strip, or a series of seven plats, was treated with manganese sulphate; the other strip of seven plats was not treated and served as a control, or check. Seven crops, rye, wheat, timothy, clover, corn, cowpeas, and potatoes, were grown on both the treated and untreated plats, which lie side by side in the two strips. The crops on the plats were not rotated, but each crop grew year after year on the same plat. The manganese sulphate was applied annually, before the crops were planted, at the rate of 50 pounds per acre. The corn, cowpeas, and potatoes were planted in the spring of each year and harvested in the fall, and the wheat and rye were planted in the fall and harvested the next July. The timothy and clover plats were planted in 1907, and the ground was again plowed and reseeded in 1909.

The results for the six years from 1907 to 1912, inclusive, are given briefly in Table I and will permit a short discussion here, the reader being referred to the earlier publications previously mentioned for the results in detail. The yields are calculated to pounds and bushels per acre and are so given in the table. The wheat and rye were not thrashed, the yield being given in weight of straw plus grain. The timothy and the clover were a failure on this soil; these plats produced practically no yield and no results were obtained.

TABLE I.—*Effect of manganese sulphate on the yields per acre of wheat, rye, cowpeas, corn, and potatoes on an acid soil treated for six successive years (1907 to 1912, inclusive).*

Year.	Wheat.			Rye.			Cowpeas.		
	Untreated.	Treated with manganese sulphate.	Increase or decrease of manganese plat.	Untreated.	Treated with manganese sulphate.	Increase or decrease of manganese plat.	Untreated.	Treated with manganese sulphate.	Increase or decrease of manganese plat.
	Pounds.	*Pounds.*	*Pounds.*	*Pounds.*	*Pounds.*	*Pounds.*	*Pounds.*	*Pounds.*	*Pounds.*
1907							8,320	6,720	−1,600
1908	4,960	4,320	− 640	5,280	4,160	−1,120	8,800	6,560	−2,240
1909	4,160	3,680	− 480	4,160	4,640	+ 480	5,920	4,480	−1,440
1910	4,000	3,520	− 480	1,920	1,600	− 320	4,320	3,360	− 960
1911	4,000	3,360	− 640	3,680	4,000	+ 320	6,720	5,600	−1,120
1912	3,840	2,400	−1,440	2,240	2,720	+ 480	3,360	3,520	− 160

Year.	Corn.						Potatoes.		
	Untreated.		Treated with manganese sulphate.		Increase or decrease of manganese plat.		Untreated.	Treated with manganese sulphate.	Increase or decrease of manganese plat.
	Stover.	Grain.	Stover.	Grain.	Stover.	Grain.			
	Pounds.	*Bushels.*	*Pounds.*	*Bushels.*	*Pounds.*	*Bushels.*	*Bushels.*	*Bushels.*	*Bushels.*
1907	9,120	60	10,400	40	+1,280	−20	221	152	−69
1908	4,160	71	3,360	51	− 800	−20	120	80	−40
1909	4,320	20	3,040	17	−1,280	− 3	181	221	+40
1910	6,240	40	4,320	23	−1,920	−17	147	96	−51
1911	4,800	40	4,000	20	− 800	−20	243	152	−91
1912	5,440	46	2,720	9	−2,720	−37	85	61	−24

Table I shows that wheat was reduced in yield each year by the manganese, the decrease varying from 480 to 1,440 pounds per acre. With rye, the yield was increased in 1909, 1911, and 1912, and was decreased in 1908 and 1910. With corn, there was a decrease each year except 1907, when the yield of stover was larger. The growth of cowpeas was also decreased, this decrease varying from 160 pounds per acre in 1912 to 2,240 pounds in 1908. Potatoes were likewise affected, there being a smaller yield in the manganese plat each year except in 1909, when there was an increase over the check plat of 40 bushels per acre.

Acidity tests of the various plats were made in 1912. The results of these determinations show that the manganese tests were made under acid conditions.

The lime-requirement determinations were made by means of the Veitch method.[1] Table II shows the amount of lime required according to this method for each plat to produce a neutral condition in the soil. The soil in each plat required approximately a ton of lime per acre. Where wheat was grown, the manganese and the untreated plats had the same lime requirement. Where rye, corn, and cowpeas were grown, the manganese plats had a higher lime requirement than the untreated plats. With rye, the manganese plat required 2,492 pounds and the untreated plat 2,136 pounds of lime per acre. With corn, the manganese plat required 2,492 pounds and the untreated plat 1,780 pounds per acre. With cowpeas, the manganese plat required 2,492 pounds and the untreated plat 2,136 pounds per acre. Where potatoes were grown, the untreated plat had a greater lime requirement than the manganese plat, the manganese plat requiring 2,451 pounds of lime per acre and the untreated plat 2,743 pounds.

TABLE II.—*Lime ($CaCO_3$) requirement per acre of the various plats, to a depth of 6 inches.*

Plats.	Wheat.	Rye.	Corn.	Cowpeas.	Potatoes.
	Pounds.	*Pounds.*	*Pounds.*	*Pounds.*	*Pounds.*
Treated with manganese	1,780	2,492	2,492	2,492	2,451
Untreated	1,780	2,136	1,780	2,136	2,743

[1] Veitch, F. P. The estimation of soil acidity and the lime requirements of soils. *In* Jour. Amer. Chem. Soc., v. 24, no. 11, p. 1120–1128. 1902.

——— Comparison of methods for the estimation of soil acidity. *In* Jour. Amer. Chem. Soc., v. 26, no. 6, p. 637–662. 1904.

OXIDATIVE POWER OF PLATS WITH AND WITHOUT MANGANESE UNDER ACID CONDITIONS.

Bertrand [1] showed that manganese played an essential part in the oxidation by the so-called oxidizing enzym laccase. Further, since manganese increased the oxidizing power of a number of soils tested by the Office of Soil-Fertility Investigations and it has been found that a number of soils of strong oxidizing power contain considerable manganese, some of which was in the highly oxidizing form of MnO_2, it became of interest to determine whether the manganese had any accelerating effect on the oxidation in the soil of the field plats planted with wheat, rye, corn, cowpeas, and potatoes.

In 1912 composite samples from five borings to the depth of 6 inches were taken of the manganese plats and check plats (1) early in April, (2) late in May, and (3) in August. The oxidation readings were made on the air-dried samples within two weeks after collection.

When 10 or 20 grams of soil are shaken two or three times with 50 to 70 c. c. of a 0.125 per cent water solution of aloin, the aloin solution is changed in a few minutes from a bright yellow to a cherry red. After the soil has stood for about an hour and has settled, the somewhat turbid solution is decanted and centrifuged, the supernatant liquid drawn off, and the depth of color of the different solutions compared by means of a Schreiner colorimeter, either with each other or with colored glass of a shade of red matching the oxidized solutions. In the present experiment the oxidation reading was made against a glass standard which matched in tint the red color produced in the aloin solution by the sample of wheat soil collected in the spring. Ten grams of soil were employed for each test. The relative oxidation in the manganese plats and the check plats is given in Table III.

TABLE III.—*Relative oxidation in plats treated with manganese sulphate and in the corresponding check plats growing the same crops (wheat soil in April being taken as 100).*

Crop.	April.		June.		August.	
	Untreated plats.	Plats treated with manganese.	Untreated plats.	Plats treated with manganese.	Untreated plats.	Plats treated with manganese.
Wheat	100	95	110	130	55	64
Rye	131	105	131	105	78	60
Corn	110	100	130	131	87	75
Cowpeas	66	64	105	110	53	53
Potatoes	87	60	91	78	53	55

[1] Bertrand, Gabriel. Sur les rapports qui existent entre la constitution chimiques des composés organiques et leur oxydabilité sous l'influence de la laccase. *In* Compt. Rend. Acad. Sci. [Paris], t. 122, no. 20, p. 1132–1134. 1896.

——— Sur l'intervention du manganèse dans les oxydations provoquées par la laccase. *In* Compt. Rend. Acad. Sci. [Paris], t. 124, no. 19, p. 1032–1035. 1897.

With the exception of the wheat plat, where there is shown a slight increase as an average of the three determinations, the addition of manganese sulphate has not increased the oxidative power of the soil, and in a number of instances it has lessened oxidation. The soil in general has a tendency to be acid in character and at best has not a strong oxidizing power. If the first determination, made in April, is considered (that is, the oxidative power of the plats at a time when there is little or no growth) the oxidation in the manganese plat is less in every instance than that of the check plat. This period is the best one for testing the oxidation effect of manganese unmodified by plant growth. The lessened oxidation produced by manganese sulphate is in harmony with the lessened yields on the same plats under treatment with manganese. In 1912, for instance, the year in which the oxidation was tested, the yield, as previously shown, of wheat, corn, and potatoes was less on the manganese plat than on the untreated plat, while rye only showed a slight increase and the yield of cowpeas was practically the same.

In the second determination, made in June, the oxidative power of the manganese plat is on the average more like that of the check plat.

In the third determination, made in August, shortly after the wheat and rye had been taken off, the manganese plat was on the average again less than the check plat.

As previously pointed out, the manganese plats, with the exception of the potato and the wheat plats, showed a higher lime requirement than the check plats. Under acid conditions the formation of organic compounds capable of acting as oxygen carriers or as activators of inorganic oxidizing compounds, such as manganese salts, is much lessened or entirely inhibited. This is also indicated from the results with the acid soil under investigation, for the addition of manganese did not increase the oxidizing power of the soil nor, indeed, of plants growing therein. This oxidizing power of the plants was tested in the case of wheat. By carefully removing the soil from the young wheat plants growing on the plats, the oxidizing power of the intact roots when placed in an aloin solution was found to be no greater in the case of the plants from the manganese plat than from the check plat. The relative oxidation was 97 and 100, respectively.

EFFECT OF MANGANESE ON ARLINGTON SOIL UNDER NEUTRAL CONDITIONS.

As the manganese had no beneficial effect on the soil under acid conditions, the experiment was continued and the soil neutralized as nearly as possible by applying lime from year to year. Three years' results have now been secured. Each year before planting, the lime requirement of the plats was determined by the Veitch method and an excess of lime added to both the check and manganese plats. The

experiment was conducted as in previous years. Manganese sulphate was applied each year in amounts of 50 pounds per acre and the same crops were grown on the same plats as before except on the clover plats, which were planted in string beans. The timothy plats were again plowed and reseeded.

In September, 1912, the plats were limed, using 500 pounds per acre $CaCO_3$ in excess of the amounts required by the soil as determined by the Veitch method, given in Table II. The manganese sulphate was applied to the wheat, rye, and timothy plats on September 15, and the plats and their checks were seeded. The corn, cowpea, bean, and potato plats received their applications in the spring of 1913, shortly before seeding time.

The results for 1913 are given in Table IV.

TABLE IV.—*Effect of manganese sulphate on the yields of wheat, rye, timothy, beans, corn, cowpeas, and potatoes in 1913.*

Area and treatment.	Wheat.	Rye.	Timothy.	Beans.		Corn.			Cowpeas.	Potatoes.	
				Pods.	Vines.	Stover.	Ears.				
Per square rod:	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Bush.*	*Lbs.*	*Lbs.*	*Bush.*
Untreated	13	15	36	15	18	24	13	.....	32	24	.....
Treated with $MnSO_4$	11	14	38	17	18	21	11	.....	29	21	.....
Per acre (calculated):											
Untreated	2,080	2,400	5,760	2,400	2,800	3,840	.....	30	5,120	.....	64
Treated with $MnSO_4$	1,760	2,240	6,080	2,720	2,800	3,360	.....	25	4,640	.....	56

The results show that the manganese sulphate has again depressed the yield, but only slightly as compared with previous years. The only cases where the manganese plats produced larger yields were with timothy and beans, but the differences are very small.

The soil was again examined for acidity early in August and the wheat, rye, corn, cowpea, and potato plats were again found to be acid; the timothy and string-bean plats, however, were neutral. This was true of both the check plat and the manganese-treated plat. The lime requirement of the different plats, expressed in pounds of $CaCO_3$ per acre, is given in Table V.

TABLE V.—*Lime ($CaCO_3$) requirement per acre of the different plats to a depth of 6 inches.*

Plats.	Wheat.	Rye.	Timothy.	Beans.	Corn.	Cowpeas.	Potatoes.
	Pounds.	*Pounds.*			*Pounds.*	*Pounds.*	*Pounds.*
Untreated	1,400	1,000	Neutral.	Neutral.	1,200	900	1,200
Treated with $MnSO_4$	1,200	1.200	...do....	...do....	700	900	900

The amounts of lime added in the fall of 1912 were not sufficient to keep this soil neutral during the next growing season except in the two cases mentioned, and it is noted that these are the two plats on which the manganese produced the increase over its check.

For the 1914 crops, lime ($CaCO_3$) was added to all the plats at the rate of 2,000 pounds per acre, except the timothy and bean plats, which received an application of 500 pounds per acre. To the timothy plats lime was added on the surface to the sod; on the other plats the lime was applied to the surface and well harrowed, so as to thoroughly mix the lime with the soil to a considerable depth. The reaction of the soil was tested four weeks after the lime was applied and periodically during the growing season. The soil in all the plats showed no acidity during the entire season.

The manganese sulphate was applied and the crops were grown in 1914 as before. The yields for the year are given in Table VI.

TABLE VI.—*Effect of manganese sulphate on the yields of wheat, rye, timothy, beans, corn, cowpeas, and potatoes in 1914.*

Area and treatment.	Wheat.	Rye.	Timothy.	Beans.		Corn.			Cowpeas.	Potatoes.	
				Pods.	Vines.	Stover.	Ears.				
Per square rod:	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Bush.*	*Lbs.*	*Lbs.*	*Bush.*
Untreated	23	37	38	17	20	28	14	.....	23	23	.....
Treated with $MnSO_4$	28	57	43	20	24	31	16	.....	27	21	.....
Per acre (calculated):											
Untreated	3,680	5,920	6,080	2,720	3,200	4,480	.....	32	3,680	.....	61
Treated with $MnSO_4$	4,480	9,120	6,880	3,200	3,840	4,960	.....	36	4,320	.....	56

Table VI shows that the manganese-treated plat with each crop except potatoes produced a larger yield than its check. The largest increase was with the rye crop. The grain was thrashed in this case, the check plat yielding 4 pounds of grain and the manganese plat $7\frac{1}{2}$ pounds. The straw was increased 3,200 pounds per acre. The rye growing on the check and manganese plats is shown in figures 1 and 2 and the harvested straw and grain in figure 3. In the case of the other crops wheat was increased 800 pounds, timothy 800 pounds, bean vines 640 pounds, bean pods 480 pounds, corn stover 480 pounds, corn grain 4 bushels, and cowpea hay 640 pounds per acre. With potatoes, there was no increase; in fact, a decrease of 5 bushels per acre is shown.

For the 1915 crop all the plats were again limed at the rate of 2,000 pounds per acre, the lime being applied in the fall of 1914. The manganese was applied as usual. Acidity tests of the soil were made periodically, and again the soil was found not to become acid during the growing season of 1915. The yields for 1915 are given in Table VII.

TABLE VII.—*Effect of manganese sulphate on the yields of wheat, rye, timothy, beans, corn, cowpeas, and potatoes in 1915.*

Area and treatment.	Wheat.	Rye.	Timothy.	Beans.		Corn.			Cowpeas.	Potatoes.	
				Pods.	Vines.	Stover.	Ears.				
Per square rod:	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Lbs.*	*Bush.*	*Lbs.*	*Lbs.*	*Bush.*
Untreated	11	18	41	25	31	48	30	.....	31	19	.....
Treated with $MnSO_4$	14	26	45	27	34	54	33	.....	40	19	.....
Per acre (calculated):											
Untreated	1,760	2,880	6,560	4,000	4,960	7,680	.....	68	4,960	.....	40
Treated with $MnSO_4$	2,240	4,160	7,200	4,320	5,440	8,640	.....	75	6,400	.....	40

The effect of manganese on all the crops in 1915 was somewhat similar to its effect in 1914. Considerable increases were produced

FIG. 1.—Rye on an untreated plat.

with each crop except potatoes. In this case the yield was the same in the check plat and manganese plat. Again the largest increase was secured with rye.

OXIDATIVE POWER OF PLATS WITH AND WITHOUT MANGANESE UNDER NEUTRAL CONDITIONS.

In July, 1915, samples of soil were taken from each plat, as previously described for the work done in 1912, in order to determine the oxidizing power. The relative oxidation in the check plats and manganese plats is given in Table VIII. The check plat in each case is taken as 100 and compared with the manganese plat growing the same crop.

TABLE VIII.—*Relative oxidation in plats treated with manganese sulphate and in the corresponding check plats growing the same crops.*

Plats.	Wheat.	Rye.	Timothy.	Beans.	Corn.	Cowpeas.	Potatoes.
Untreated	100	100	100	100	100	100	100
Treated with manganese	283	132	75	109	76	107	105

With the exception of the timothy and corn plats, the addition of manganese sulphate has increased the oxidizing power of the soil. In general, however, this increased oxidation agrees with the increased yields in the limed soil. This is in contrast to the action of manganese in this soil while under acid conditions, which caused less oxidation in the soil and a decreased growth. Under acid conditions the

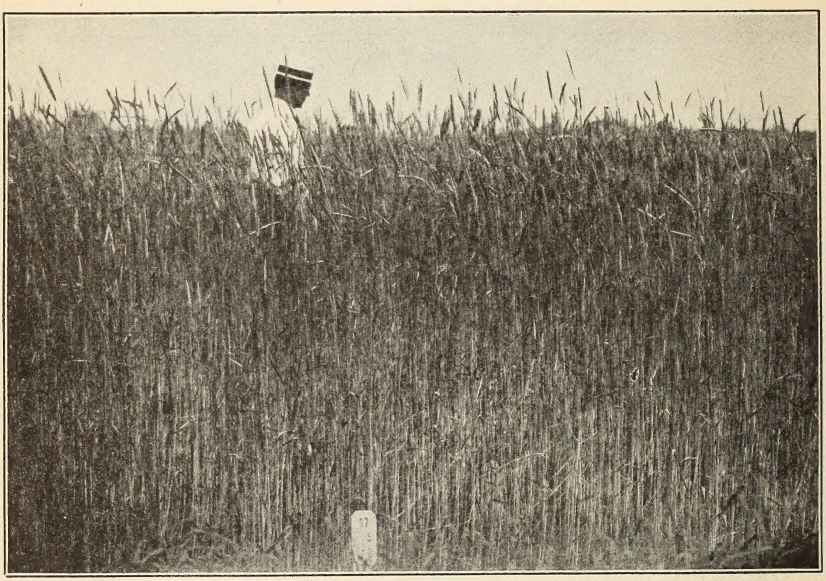

FIG. 2.—Rye on a plat treated with manganese.

effect of oxidizing compounds, such as manganese salts, is much lessened or entirely inhibited, while under neutral or slightly alkaline conditions this oxidizing power is stimulated. The soil under study is of an acid character, naturally poor in its oxidizing power, and is physically bad. Methods of cultivation which loosen and aerate the soil and chemicals which increase its oxidizing power should increase its crop-producing power. With the acid soil, where manganese gave decreased yields, conditions were such that stimulating action on plants and microorganisms of the soil did not come into play; or, possibly on account of the acidity of the soil, the effect of the manganese led to a stimulation of other biological processes,

acting on the organic soil constituents in such a manner as to produce changes injurious to the growing crops.

The stimulation of the oxidative processes by manganese was favorable in the soil kept under neutral or alkaline conditions by applying lime year by year, and these oxidative processes acting in turn on the organic or inorganic constituents of the soil produced changes beneficial to the growing crops.

SUMMARY.

In a 6-years' field test of manganese sulphate used at the rate of 50 pounds per acre on an acid silty clay loam, its effect each year

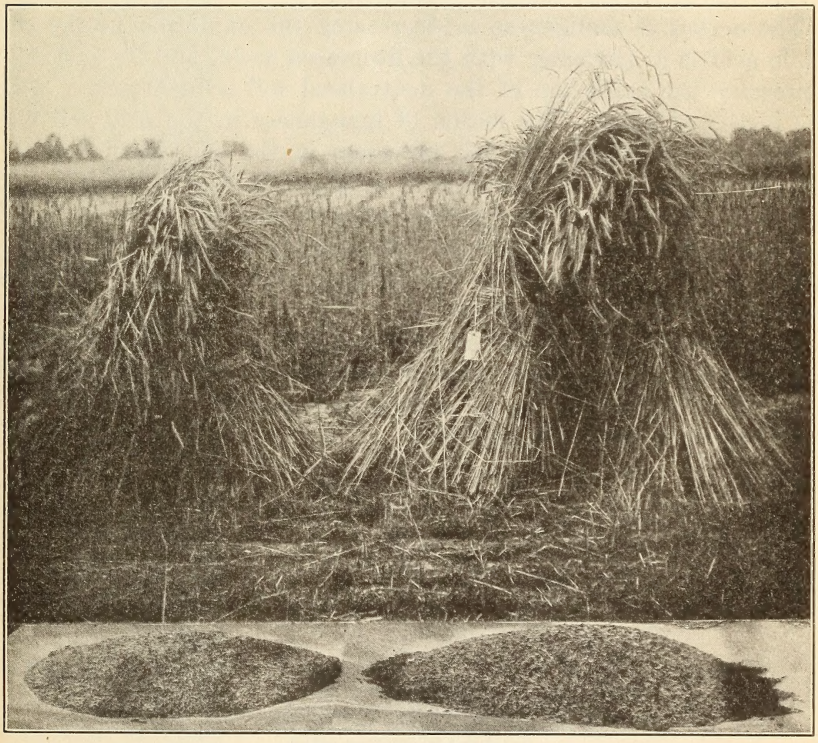

FIG. 3.—Effect of manganese on rye. Straw and grain from check plat, on the left; from plat treated with manganese, on the right.

was not beneficial to the crops grown—wheat, rye, corn, cowpeas, and potatoes. The soil in the various plats required from 1,780 to about 2,750 pounds of $CaCO_3$ to neutralize the first 6 inches. The soil is of an acid character, is low in organic matter, rather bad physically, and naturally has a poor oxidizing power. The oxidative processes in the soil were lessened by manganese in most of the plats under the acid condition.

The action of manganese was studied on the same plats, kept neutralized with lime for the three succeeding years following the experiment with the soil in an acid condition.

The productivity of the soil was increased by manganese under this neutral or slightly alkaline condition. With wheat, rye, timothy, beans, corn, and cowpeas the yields were increased, while with potatoes the yield was practically the same in the treated and the check plats.

The oxidative power of the neutralized soil was also increased by manganese, which is in accord with the results of former investigations, which have shown that the oxidation by manganese salts is greater under slightly alkaline conditions.

The action of manganese in decreasing the oxidation in the soil while acid is in harmony with the decreased yield, and its action in increasing the oxidation of the neutralized soil is in harmony with the increased yield. The action of manganese in the acid soil was probably to stimulate the life processes in the soil, acting on the organic matter in such a way as to produce changes which resulted in a lessened crop-producing power, while its action in the neutralized soil was such as to stimulate oxidation and other biological processes, acting on the organic soil constituents and producing changes favorable to the growing plants.

These results on the behavior of manganese as a so-called catalytic fertilizer when acting under acid or neutral soil conditions show that no profitable return is to be expected in soils of a persistent acid tendency until such soils are limed.

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